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NEW POLYMERS FROM NITRILOTRIACETO-  
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15 Claims

## ABSTRACT OF THE DISCLOSURE

Polymers of nitrilotriacetonitrile and iminodiacetonitrile alone and in combination have been prepared. These polymers on pyrolysis yield electrically conducting materials having the same general shape as the starting prepolyzed material.

This invention relates to producing novel polymers from nitrilotriacetonitrile, iminodiacetonitrile and mixtures of nitrilotriacetonitrile and iminodiacetonitrile. It further relates to pyrolyzing these polymers to produce a product that is electrically conductive.

Polymeric nitriles produced from a single nitrile monomer or from two different nitrile monomers by nitrile group reaction is new to the art. It has been known to coreact formaldehyde with an amino hydrogen containing aminonitrile to produce polymeric condensation products. However, such products are soft and are soluble in organic solvents, acids and bases. In contrast, the nitrile polymers of the present invention are insoluble in all of the common organic solvents and in acids and bases. They are also hard and highly heat resistant.

The heat resistance of these polymers coupled with inertness to organic and aqueous solvents make these polymers useful catalyst carriers or insulators. The monomers can be melt reacted in a mold having the final shape desired. It is also within the present invention to solution polymerize. This polymerization yields a particulate solid which is compressed to a final shape. Also, fillers such as metal or metal oxide powders and filaments can be added during polymerization which will be embedded in the final polymer matrix. These polymers will be useful as furnace insulation and as potting materials for thermocouples and thermistors. By being inert to organic solvents and aqueous solutions, the use of articles fabricated from these polymers will not be restricted by environmental conditions.

Another use of these novel polymers is in the production of electrically conducting substances. On pyrolysis of these polymers of iminodiacetonitrile, nitrilotriacetonitrile and mixtures of iminodiacetonitrile and nitrilotriacetonitrile, a polymeric electrically conductive composition is formed. These compositions are carbon, hydrogen, oxygen and nitrogen containing substances and can be produced in any shape or size. To produce a desired shape, it is only necessary to use a mold of that shape during nitrile polymerization if a melt process is used. In solution polymerization, the polymer can be cast or extruded to a shape. After polymerization, the shape has been defined and pyrolysis can take place within the mold or with the surfaces exposed. These hard compositions are useful as current collecting brushes or can be used in semiconductor applications.

Conductive carbonaceous materials have been produced by pyrolysis of polymeric materials. However, the polymers pyrolyzed have been mainly carbonaceous to produce graphitic conductive polymers. Polyacrylonitrile has also been pyrolyzed to produce electrically conductive polymers. However, the electrically conductive polymers

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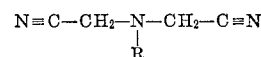
of the present invention are heat stable and have a high nitrogen content. This high percentage of bonded nitrogen increases the hardness and thermal stability of these conductive polymers. It is also possible to readily produce shaped conductive polymers.

It is an object of this invention to produce novel polymers from a monomer nitrile or a mixture of monomer nitriles.

It is also an object of this invention to produce novel electrically conductive polymers.

It is further an object of this invention to set out a method of polymerizing organonitriles by nitrile group reaction.

More specifically, this invention relates to polymerization of nitrile monomers having a structure



wherein R is selected from the group consisting of hydrogen, and  $-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{N}$ . These nitriles can be polymerized in a molten state or in a solvent. A base catalyst is used to initiate reaction in either condition. The polymerizations are conducted in air or an inert atmosphere with little variation in results. The polymers formed are dark non-melting insoluble polymeric solids with good resistance to thermal degradation. On pyrolysis of these polymers at from about 500° C. to about 1500° C. hard dark carbonaceous solids containing carbon, hydrogen, oxygen and nitrogen are produced. These pyrolyzed solids, which retain the same general shape as the starting polymer, have an electrical resistance of from about 10<sup>13</sup> ohm-cm. to about 38 ohm-cm.

The monomers of this invention are known substances as to their properties and synthesis. Iminodiacetonitrile was first produced in 1894 by the reaction of hexamine with hydrogen cyanide under acid conditions. Pure iminodiacetonitrile is a white solid melting at 78° C. Nitrilotriacetonitrile is produced by the reaction of hexamethylenetetramine with formaldehyde and hydrocyanic acid in the presence of sulfuric acid. The mole ratio of reactants is 1:6:12 respectively and the pH is maintained at about 1. Nitrilotriacetonitrile is produced in good yield.

Broadly, the polymerization of iminodiacetonitrile (IDAN), nitrilotriacetonitrile (NTAN) or mixtures of these monomers can be carried out at from about 0° C. to about 200° C. More ideally, the polymerization temperature is maintained at from about 70° C. to about 165° C. when polymerization is from the melt; and from about 20° C. to about 90° C. for polymerization from solution. The suitable solvents for solution polymerization are organic alcohols, ethers, esters, amides, sulfoxides and aromatic hydrocarbons. The preferred solvents consist of methanol, ethanol, isopropanol, butanol, tetrahydrofuran, 1,2-dimethoxyethane, diethylene glycol, dimethylether, benzene, toluene, xylene, mono- and dichlorobenzene, chloroethylene, mineral oil and decalin.

The basic catalysts are used for both polymerization from the melt and from solution. Suitable base catalysts are the metal hydrides, alkaline hydroxides, alkoxides, alkaline cyanides, alkaline alkyls and amines. The preferred base catalysts are the alkoxides of sodium, especially sodium methoxide; the cyanides of sodium and potassium; lithium alkyls and diamines such as N,N-bis-cyclohexamethylene diamine (DABCO). Other secondary amines and also primary and tertiary amines produce polymers in good yields. In the melt polymerization the catalyst is added in a solvent which is then removed.

The time for polymerization depends mainly on whether polymerization is from the melt or from a solution. Polymerizations from the melt generally vary from 1 to 16 hours, while polymerizations from solution generally re-